

Rotational Far Infrared Spectrum of $^{13}\text{CO}^1$

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The pure rotational spectrum of ^{13}CO between 0.66 and 3.3 THz has been measured with a tunable far infrared spectrometer. Revised values for B_0 , D_0 , and H_0 have been obtained with a 1σ standard deviation of 50 kHz. Additional measurements were performed with a Fourier transform spectrometer, and a 1 MHz ($3.3 \times 10^{-5} \text{ cm}^{-1}$) measurement accuracy is demonstrated with this device. The rotational spectrum from $J'' = 0$ to $J'' = 30$ is calculated and gives the frequencies with a 1σ uncertainty of less than 120 kHz. © 1990 Academic Press, Inc.

INTRODUCTION

State-of-the-art Fourier transform spectrometers (FTS) can now achieve a resolution on the order of 10^{-3} cm^{-1} with an accuracy of 10^{-4} cm^{-1} (1, 2). Even higher resolution and accuracy can be achieved with two recently developed laser based techniques. The first of these is the generation of microwave sidebands on the strongest FIR laser lines in Schottky diodes (3-6); it produces tunable FIR radiation up to about 3 THz (100 cm^{-1}) with 5 kHz linewidths and roughly 500 kHz accuracy. The second method is the nonlinear mixing of CO_2 laser radiation in metal-insulator-metal diodes (7), producing tunable FIR radiation up to 6 THz (200 cm^{-1}) with 10 kHz linewidths and 35 kHz accuracy. This latter technique has provided accurate frequency markers for calibrating FTS spectra (8) and made it possible to obtain an accuracy with FTS devices of a few MHz (2).

We have used a tunable FIR spectrometer in combination with a high-resolution FTS to measure the pure rotational spectra of the carbon 13 isotope of carbon monoxide. The observations of ^{13}CO FIR transitions play an important role in determining the physical and chemical properties of interstellar molecular clouds (9). The observation of both ^{13}CO and ^{12}CO will shed light on the $^{13}\text{C}/^{12}\text{C}$ abundance ratio and may also provide a better measurement of the cloud temperature than the ^{12}CO FIR observations. Despite this, the only previous high resolution work on these spectra was the measurement of the $J = 1-0$ microwave transition (10); all other transitions were predicted from the isotopically scaled ^{12}CO molecular constants. Moreover, the ^{13}CO rotational spectra consist of single, well resolved transitions of reasonable intensity

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and hence can provide a good test of the accuracy achievable with our new FTS without the additional complications of poor signal-to-noise ratio or unresolved lines. The measurements with the tunable FIR system then serve as a direct check on the FTS accuracy.

EXPERIMENTAL DETAILS

1. Tunable FIR Measurements

Our newly constructed tunable FIR (TuFIR) spectrometer generates FIR radiation by the nonlinear mixing of three radiations (two from CO_2 lasers and one from a microwave source) in a third-order metal-insulator-metal (MIM) diode (7, 8). The MIM diode generates microwave sidebands on the CO_2 difference frequency; that is,

$$\nu_{\text{FIR}} = (\nu_{\text{I}} - \nu_{\text{II}}) \pm \nu_{\mu\text{w}},$$

where ν_{FIR} is the generated far infrared frequency, ν_{I} and ν_{II} are the laser frequencies, and $\nu_{\mu\text{w}}$ is the microwave frequency.

Figure 1 is a schematic of the third-order TuFIR spectrometer at LENS. The radiation from lasers I and II is combined on a beamsplitter and coupled onto the diode by a 25-mm focal length lens. The microwave radiation is coupled onto the diode by a bias tee connected to the diode junction. The generated FIR is radiated from the diode's whisker in a long wire antenna pattern (11). This FIR radiation is then collected and collimated by a 30-mm focal length off-axis section of a parabolic mirror. After passing through an absorption cell the FIR is detected on a liquid He-cooled Si bolometer. The FIR radiation is frequency modulated (by frequency modulation of the CO_2 lasers) and detected in a lock-in amplifier.

The far infrared frequency is tuned by scanning the microwave frequency. This is controlled by a personal computer, which also collects the data from the lock-in amplifier. Thus, we are able to average scans for increased sensitivity. This is essentially the same experimental arrangement as described in Ref. (8) but without the acousto-optic modulators isolating the lasers from the diode.

The frequency range of the spectrometer is 0.3 to 6 THz. The lower limit is set by our bolometer and the upper limit by the largest difference frequency between $^{12}\text{C}^{16}\text{O}_2$

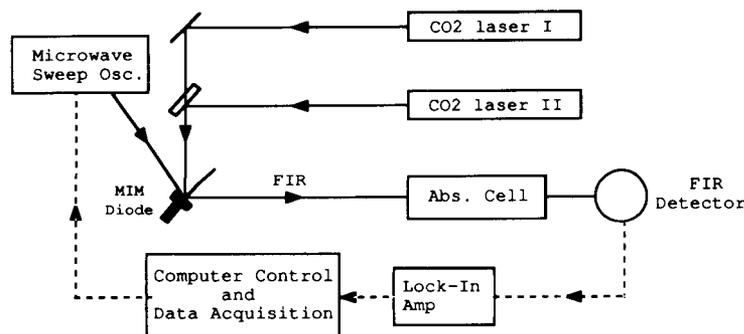


FIG. 1. Schematic diagram of the tunable far-infrared spectrometer at LENS. The generated FIR frequency is $\nu_{\text{FIR}} = (\nu_{\text{I}} - \nu_{\text{II}}) + \nu_{\mu\text{w}}$, and is in the range of 0.3 to 6 THz.

lasers. Over 100 lines oscillate on each CO₂ laser; with ± 20 GHz tunability from the microwave sweeper, a 95% coverage of this region is obtained (the gaps occur only above 4.5 THz). Both CO₂ lasers are frequency stabilized to the 4.3 μm saturated fluorescence signal from low-pressure CO₂ cells (12) (not shown in Fig. 1). These frequencies have been measured to an absolute frequency with an uncertainty less than 5 kHz (13, 14). Without using special locking techniques described in Refs. (13, 14), our measured stability is 25 kHz for each laser. The overall frequency uncertainty of our FIR radiation is thus $\sqrt{2} \times 25$ kHz or 35 kHz.

The spectrometer sensitivity is limited by the FIR power and the sensitivity of the detector. FIR powers of 10^{-8} to 10^{-7} W are generated with 150 mW from each laser and 6–10 dBm of microwave power applied to the MIM diode. For the best contacts, our minimum detectable absorption is 10^{-4} using a 1-sec integration time (for a meter-long cell the minimum detection coefficient is thus 10^{-6} cm^{-1}).

The MIM diode consists of an electrochemically sharpened tungsten whisker (25 μm diameter and 3 to 7 mm long) contacting a metal base. The metal base has a naturally occurring thin oxide insulating layer. Both nickel and cobalt have been used as base materials, but cobalt is generally more consistent in the production of third-order FIR radiation.

For the present experiment the absorption cell consists of a 24-mm ID Pyrex tube, 0.5 m long with high density polyethylene windows. An enriched sample of ¹³CO

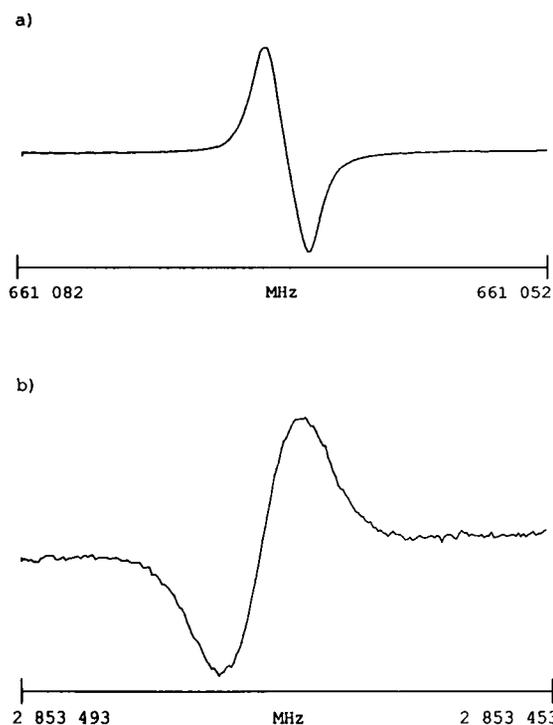


FIG. 2. The a) $J = 6-5$ and b) $J = 26-25$ transitions of ¹³CO measured with the tunable FIR spectrometer.

(99% isotopically pure) was used at a pressure of 70 to 350 mTorr, depending on the strength of the transition. In Fig. 2 are recordings of the $J = 6-5$ and $J = 26-25$ transitions. In all, eight lines were measured, extending to the $J = 30-29$ transition at 3.3 THz; the observed frequencies are listed in Table I and the 1σ uncertainty of these values is given in parenthesis. This uncertainty is the quadrature sum of the 35-kHz FIR uncertainty with the uncertainty of determining the absorption line center (which depends on the linewidth and the signal-to-noise ratio).

2. Fourier Transform Spectrometer Measurements

The FTS was operated with the maximum optical path difference of 2.7 m and a corresponding unapodized resolution full width at half maximum of less than $1.5 \times 10^{-3} \text{ cm}^{-1}$ (45 MHz). A silicon composite bolometer detector operating at 4.2 K was used. A cooled filter of crystal quartz coated on one side with Garnet powder limited the radiation on the bolometer to the region below 100 cm^{-1} . The spectra were obtained in a single run of 24 h.

The sample cell was a 20-cm-long Pyrex tube fitted with 0.8-mm-thick high-density polyethylene windows. It was filled with a 1:1 mixture of ^{13}CO and ^{12}CO to a total pressure of 500 Pa (3.7 Torr). Mixing the two isotopes allowed us to calibrate the

TABLE I
Measured Rotational Transition Frequencies of ^{13}CO

$J'-J''$	TuFIR (MHz) ^a	FTS (MHz) ^b	FTS (cm^{-1})
6-5	661 067.276 (50)		
7-6		771 182.4	25.723 877
8-7		881 274.1	29.396 141
9-8		991 328.7	33.067 166
10-9		1 101 347.4	36.736 994
11-10	1 211 329.636 (50)	1 211 329.5	40.405 603
12-11		1 321 265.8	44.072 683
13-12		1 431 152.7	47.738 117
14-13		1 540 988.2	51.401 835
15-14	1 650 767.344 (55)	1 650 767.8	55.063 687
16-15		1 760 485.8	58.723 486
17-16		1 870 139.6	62.381 142
18-17		1 979 726.5	66.036 567
19-18	2 089 240.033 (55)	2 089 240.0	69.689 544
20-19		2 198 676.8	73.339 965
21-20		2 308 035.5	76.987 778
22-21		2 417 308.7	80.632 739
23-22		2 526 491.6	84.274 687
24-23		2 635 584.0	87.913 620
25-24	2 744 579.059 (60)	2 744 578.8	91.549 293
26-25	2 853 474.444 (60)		
28-27	3 070 948.140 (70)		
30-29	3 287 972.525 (100)		

^a The 1σ uncertainty of the experimental measurements is shown in parentheses.

^b The 1σ uncertainty of all FTS measurements set at 1 MHz.

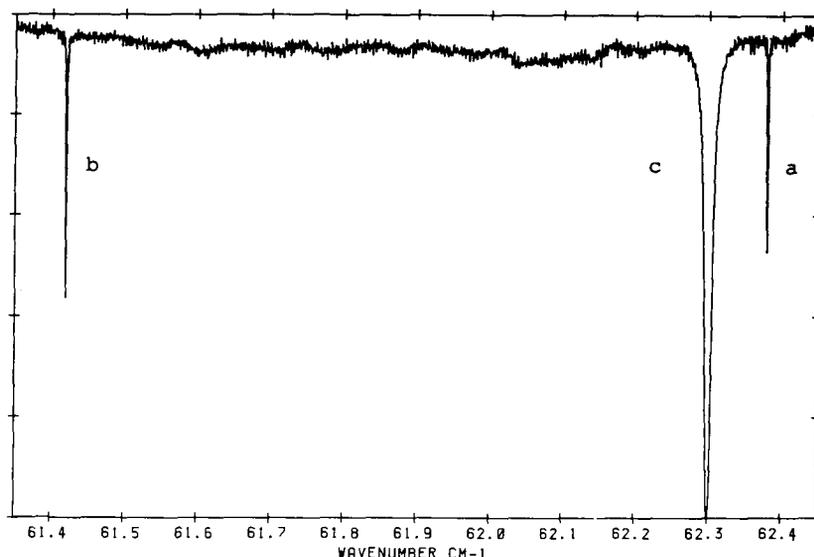


FIG. 3. Fourier transform spectrometer recordings: a) the $J = 17-16$ ^{13}CO transition, b) the $J = 16-15$ ^{12}CO transition used for calibration, and c) a residual water vapor transition.

^{13}CO spectra with the accurately measured ^{12}CO transitions (8). To calibrate the spectrometer the differences between ^{12}CO frequencies of Ref. (8) and those measured by the FTS system were plotted against the line frequency. These data were fitted to a straight line passing through 0, 0 by a least-squares routine. The rms deviation of the fit was 700 kHz (1σ).

The complete list of the observed transition frequencies is presented in Table I. All of the transitions were well isolated from strong water lines (present as a contaminant in the spectrometer), and hence the determination of the line center is limited only by the signal-to-noise ratio. Figure 3 shows the $J = 17-16$ ^{13}CO line together with the $J = 16-15$ ^{12}CO calibration line and a water vapor transition. The signal-to-noise ratio (peak-to-peak noise) for this measurement and for other strong lines was about 20:1.

ANALYSIS

The 23 measured FIR transitions were combined with the previously measured microwave transition. These frequencies were fitted to the usual energy expression for the rotational levels of a $^1\Sigma$ diatomic molecule,

$$E(J) = B_0J(J+1) - D_0J^2(J+1)^2 + H_0J^3(J+1)^3 + \dots \quad (1)$$

The best values for the parameters B_0 , D_0 , and H_0 were determined by a weighted linear least-squares routine in which the weights were proportional to the inverse of the experimental uncertainties. The uncertainty for the FTS measurements was set at 1 MHz³ ($3.3 \times 10^{-5} \text{ cm}^{-1}$). The derived parameters and their 1σ uncertainties are

³ This 1-MHz uncertainty is slightly higher than the 700-kHz uncertainty of the calibration fit. When the molecular constants B_0 and D_0 are fit to the FTS data only, the 1σ rms deviation of the fit is 870 kHz. In the final fit, the rms of obs-calc for the FTS data only is 900 kHz.

TABLE II
 Calculated ^{13}CO Rotational Frequencies and Derived Molecular Constants (MHz)

$J'-J''$	WAVENUMBERS ^a	MHz ^a	OBS-CALC (MHz)
1-0	3.675 9215 (3)	110 201.36 (1)	+0.01 ^b
2-1	7.351 7088 (3)	220 398.69 (1)	
3-2	11.027 2276 (3)	330 587.97 (1)	
4-3	14.702 3437 (7)	440 765.17 (2)	
5-4	18.376 9229 (7)	550 926.29 (2)	
6-5	22.050 8309 (7)	661 067.28 (2)	0.00 ^c
7-6	25.723 934 (1)	771 184.13 (3)	-1.73
8-7	29.396 097 (1)	881 272.81 (3)	+1.29
9-8	33.067 186 (1)	991 329.31 (3)	-0.61
10-9	36.737 068 (1)	1 101 349.60 (3)	-2.20
11-10	40.405 608 (1)	1 211 329.67 (3)	-0.03 ^c
12-11	44.072 673 (1)	1 321 265.49 (3)	+0.31
13-12	47.738 127 (1)	1 431 153.04 (3)	-0.34
14-13	51.401 837 (1)	1 540 988.32 (3)	-0.12
15-14	55.063 670 (1)	1 650 767.31 (3)	+0.03 ^c
16-15	58.723 492 (1)	1 760 485.99 (3)	-0.19
17-16	62.381 167 (1)	1 870 140.35 (3)	-0.75
18-17	66.036 564 (1)	1 979 726.39 (3)	+0.11
19-18	69.689 548 (1)	2 089 240.09 (3)	-0.06 ^c
20-19	73.339 985 (1)	2 198 677.45 (3)	-0.65
21-20	76.987 743 (1)	2 308 034.47 (4)	+1.03
22-21	80.632 687 (1)	2 417 307.14 (4)	+1.56
23-22	84.274 684 (1)	2 526 491.46 (4)	+0.14
24-23	87.913 600 (1)	2 635 583.44 (4)	+0.56
25-24	91.549 303 (1)	2 744 579.08 (4)	-0.02 ^c
26-25	95.181 661 (1)	2 853 474.40 (4)	+0.04 ^c
27-26	98.810 537 (1)	2 962 265.40 (4)	
28-27	102.435 802 (2)	3 070 948.09 (5)	+0.05 ^c
29-28	106.057 321 (2)	3 179 518.49 (6)	
30-29	109.674 961 (3)	3 287 972.62 (9)	-0.10 ^c
31-30	113.288 591 (4)	3 396 306.51 (12)	
$B_0 = 55\ 101.0128(23)$		Correlation	1.00
$D_0 = 0.167\ 6860(50)$		Matrix	0.89 1.00
$H_0 = 1.505(33) \times 10^{-7}$			0.77 0.97 1.00

^a Numbers in parentheses are 1σ uncertainties of the last digits. Wavenumbers are in cm^{-1} .

^b Observed value from Ref. (10).

^c Measured with the tunable FIR spectrometer; all other observed frequencies measured with the Fourier transform spectrometer.

presented in Table II along with a calculation of the 31 lowest rotational transition frequencies. The 1σ standard deviation of the final fit was 50 kHz; the 1σ uncertainties of the predicted frequencies range from 10 to 120 kHz.

The new constants in Table II are in agreement with the previous values (15) but are about one order of magnitude more accurately determined. This is the first direct measurement of D_0 and H_0 ; the previous value for D_0 was obtained by scaling the value for ^{12}CO . The value determined here is 20 times more accurate. H_0 was required to fit the data within the measurement error, and the value from the fit is essentially the same as that obtained by scaling the ^{12}CO H_0 value of Ref. (8) by the cube of the ratio of the reduced masses.

CONCLUSION

We have measured the pure rotational far infrared spectra of the ^{13}CO isotopomer. These measurements are derived from a state-of-the-art Fourier transform spectrometer (16) and a tunable far-infrared spectrometer. The FTS measurements were simultaneously calibrated with ^{12}CO transitions and achieved a measurement accuracy of 1 MHz ($3.3 \times 10^{-5} \text{ cm}^{-1}$). This accuracy is slightly better than that reported by Carli *et al.* in Ref. (1) and by Johns in Ref. (2), and demonstrates the high accuracy achievable with present-day Fourier transform spectrometers. However, the resolution and accuracy of the tunable spectrometer is still 10 to 50 times better, being limited, at present, by the Doppler width of the transitions.

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